Physica B 163 (1990) 69–74
North-Holland

# MAGNETIC ORDER AND SPIN FLUCTUATIONS IN OXIDE SUPERCONDUCTORS

J.W. LYNN
*Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, MD 20742, USA*
*National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

*Invited paper*

A brief review is given of both the rare earth ($\mathcal{R}$) and Cu magnetism in the $\mathcal{R}Ba_2Cu_3O_{6+x}$, $\mathcal{R}Ba_2Cu_4O_8$, $(La\text{-}Sr)_2CuO_4$ and $(Nd\text{-}Ce)_2CuO_4$ systems. The Cu magnetism is dominated by the strong in-plane exchange interactions, which give rise to two-dimensional magnetic behavior in both the antiferromagnetically ordered insulating phase as well as in the superconducting state. The rare earth ions, on the other hand, order at low temperatures irrespective of the presence or absence of superconductivity. In the 1-2-3 and 2-4-8 materials, 2-d behavior is observed, while in the $(Nd\text{-}Ce)_2CuO_4$ system there is a substantial magnetic interaction between the Nd and Cu sublattices.

## 1. Introduction

The superconducting oxides exhibit a rich variety of cooperative phenomena, including metal–insulator transitions, antiferromagnetism, and of course superconductivity. From the standpoint of superconductivity the central issue is to identify the nature of the superconducting state. One aspect concerns the basic character of the superconducting state itself, that is, whether it develops in the usual BCS way as a result of an instability of the Fermi liquid, or perhaps entails a different mechanism such as RVB. The second basic question involves the identification of the interaction which is responsible for the electron pairing. The magnetic properties of these oxide materials have been of particular interest since the discovery that the Cu ions carry an unpaired spin, with the consequent possibility that the magnetic fluctuations may be responsible for the superconductivity.

A second aspect concerns the magnetism of the rare earths. Some of the very first data on the $\mathcal{R}Ba_2Cu_3O_{6+x}$ ($\mathcal{R}$ = rare earth) compounds showed that substitution of the trivalent rare earths had little effect on the superconducting properties [1], and this has also been found to be the case for the $\mathcal{R}Ba_2Cu_4O_8$ system [2]. Hence the rare earth sublattice is electronically isolated from the superconducting (Cu–O) sublattices, leading to magnetic ordering of the rare earth ions at very low temperatures ($\leqslant 2$ K) just like conventional "magnetic-superconductor" systems [3]. The tetravalent rare earths (Ce, Pr, Tb), on the other hand, are more strongly coupled to the rest of the electronic system. The superconducting transition temperature is found to decrease strongly with increasing substitution of these elements [4], and the magnetic ordering temperatures are much higher than for the trivalent rare earths [5].

Here we will very briefly review some of the highlights of the magnetic properties of these systems, as discussed in the High-$T_c$ Superconductivity Experimental Panel. A more complete review of the properties of the oxide superconductors, with extensive references to the literature, can be found in ref. [6].

## 2. Cu magnetism

The first evidence for magnetic ordering of the Cu ions in these systems was obtained for $La_{2-x}Sr_xCuO_4$ by susceptibility [7], neutron scattering [8], and muon precession [9] experiments, followed by measurements on the $\mathcal{R}Ba_2Cu_3O_{6+x}$ system [10], and more recently, the $(Nd_{1-x}Ce_x)_2CuO_4$ system [11]. The overall behavior of the magnetic and superconducting properties as a function of $x$ are quite similar, and the basic phase diagram for the $\mathcal{R}Ba_2Cu_3O_{6+x}$ system is shown in fig. 1. At small $x$ the Cu spins order antiferromagnetically in the semiconducting phase, with Néel temperatures $T_N$ as high as 500 K. This is a very high ordering temperature for an insulating magnet. Moreover, above the 3-d ordering temperature very strong spin correlations persist within the Cu–O planes, with a magnetic energy scale which is an order of magnitude larger than $T_N$ would indicate [12]. The existence of these large magnetic energies has fueled speculation

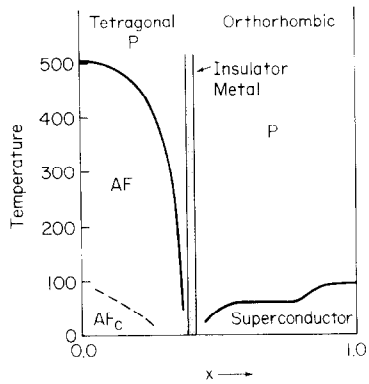


Fig. 1. Schematic phase diagram for $\mathcal{R}Ba_2Cu_3O_{6+x}$ as a function of oxygen concentration $x$ on the "chain" sites. The paramagnetic (P) and antiferromagnetic (AF) phases are shown, as well as an antiferromagnetic phase found at lower temperatures ($AF_c$), where the spins on the Cu chains order.

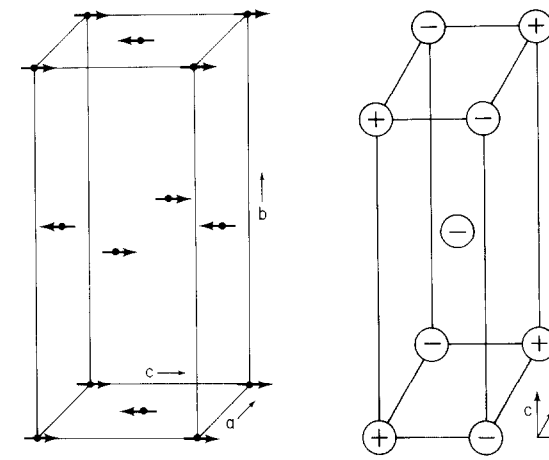


Fig. 2. Copper spin structures for (left) $La_2CuO_4$ and (right) $Nd_2CuO_4$.

that this is the energy scale needed for the high superconducting transition temperatures $T_c$. This possibility has been further supported by the observations that the magnetic fluctuations survive into the superconducting phase which is found at higher $x$ [12, 13], and also by the discovery that the temperature dependence of these fluctuations is directly affected by the superconducting transition [13]. However, the question of the origin of the superconductivity has by no means been settled yet. Nevertheless, even if magnetism is not the origin of the superconductivity in these high-$T_c$ materials, it is quite clear that the Cu–O layers are intimately involved in both the magnetism and superconductivity, and the striking magnetic behavior these materials display is of fundamental interest in its own right.

In all of these systems, for both the Cu magnetic order as well as the rare earth magnetic order, the spin structures are relatively simple commensurate antiferromagnetic configurations. By commensurate we mean that the magnetic unit cell is a simple integer multiple of the chemical unit cell: most often the magnetic unit cell is just twice the size of the chemical unit cell to accommodate the antiparallel arrangement of spins in the antiferromagnetic structure. However, there is the complication that some of the structures are noncollinear, by which we mean that the spins do not necessarily point along the same crystallographic direction. The basic magnetic structures for the Cu ordering are shown in fig. 2 for $La_2CuO_4$ [8] and $Nd_2CuO_4$ [11], and fig. 3 for the $\mathcal{R}Ba_2Cu_3O_{6+x}$ system [10].

The observed spin structure for $La_2CuO_4$ (left side of fig. 2) consists of ferromagnetic sheets of spins in the $b$-$c$ plane, with adjacent sheets arranged antiparallel. Note that here the tetragonal axis is designated as $b$. The Néel temperature is ~300 K, but the Cu–Cu exchange interaction within the $a$-$c$ plane is mediated by the intervening O ions, and the directional Cu–O bonding yields an exchange interaction which is much larger than the exchange interaction between planes, and much larger than $kT_N$ would suggest. It is the anisotropy of the Cu–O bonding in all these systems that gives rise to the large energy scale and the 2-d like behavior for the Cu magnetism.

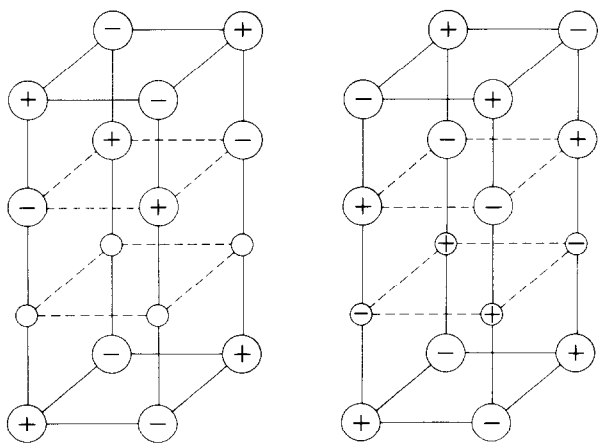

Fig. 3. On the left is the magnetic spin configuration for the Cu moments in the high temperature ordered phase ($T_{N2} < T < T_{N1}$). The large circles represent the copper ions in the Cu planes, and the smaller circles represent the Cu in the "chain" layer. In this phase there is no ordered moment in the chain layer. On the right is shown the spin configuration in the low $T$ phase when the Cu chains order.

The basic spin structure for the Cu spins in $Nd_2CuO_4$ is shown on the right hand side of fig. 2. It is very similar to $La_2CuO_4$ [14]. Initial polarized beam data [11] suggested that the spins in adjacent layers were not collinear in this structure, but a collinear structure with the spin direction initially along the [1 1 0] can also explain the data. The magnetic ordering occurs at ~250 K, but there is a delicate balance of interactions, as a spin reorientation occurs at 75 K, and again at 30 K. These spin reorientations are not observed in $Pr_2CuO_4$ [11]. There are also two magnetic phase transitions observed at low temperatures, with at least one associated with the ordering of the Nd, and there is a small structural distortion of the system as well. Thus $Nd_2CuO_4$ is a very rich material to investigate.

For the 1-2-3 system there are three copper–oxygen layers of ions in each chemical unit cell which are stacked along the $c$-axis. Two of these layers have oxygen ions between the Cu ions in both the $a$ and $b$ crystallographic directions (the Cu-plane layers), and the oxygens cannot be removed. The third Cu layer only has O ions along one axis. This is the so-called chain layer, and the oxygen concentration can be readily varied in this layer from full occupancy ($x = 1$) to full depletion ($x = 0$). Both the magnetic and superconducting properties are a very sensitive function of the oxygen concentration $x$ in this 'chain" layer as shown in fig. 1. In the fully oxygenated case ($x = 1$) the system is a $90^+$ K superconductor for all the trivalent rare earth elements $\mathcal{R}$. In the magnetic regime ($x \lesssim 0.4$) there are two separate transitions to long range antiferromagnetic order of the Cu spins which have been observed. The high temperature transition involves ordering in the Cu-plane layers, and has a Néel temperature $T_{N1}$ which is ~500 K at $x = 0$, and monotonically decreases to zero at $x \sim 0.4$. The spin structure is shown in the left portion of fig. 3, and we see that nearest neighbor spins both within the Cu-planes, as well as along the $c$-axis, are arranged in a simple antiparallel configuration. The spin direction lies in the $a$-$b$ plane. One of the interesting aspects of this ordering is that $T_{N1}$ appears to be very sensitive to pressure [15].

At lower temperatures the Cu spins in the "chain" layers have also been observed to order, and the spin structure is shown on the right side of fig. 3. However, unlike the high temperature phase just discussed, where the same spin configuration has been observed in many different samples independent of oxygen concentration, the chain ordering appears to be very sensitive to the chemical and metallurgical state of the sample. Hence the phase boundary as a function of oxygen concentration has not been established, and indeed it is not even clear if a universal curve is appropriate. This is an area where considerably more work needs to be done.

The ordering of the chain ions causes an interesting problem for the spin system. Within the chain layer the nearest neighbor spins are again aligned antiparallel just like the Cu-plane layers, but as we proceed along the $c$-axis the spins in all the layers want to be aligned antiparallel. If one compares the two structures in fig. 3, we see that having the chain spins *and* the plane spins simultaneously antiparallel along the $c$-axis is not possible; hence there must be a competition between these interactions. Indeed just below the chain ordering temperature the chain spins point perpendicular to the (antiparallel) plane spins, so that the spin configuration is noncollinear. As the ordered moment develops on the chains, the plane spins rotate, and as $T \rightarrow 0$ a collinear spin structure with the configuration shown on the right is realized.

In addition to investigations of the magnetic order of the Cu spins, considerable information has been obtained about the spin dynamics both by neutron [12, 16] and Raman [13] scattering. For the $La_2CuO_4$ and $YBa_2Cu_3O_6$ ordered antiferromagnets, the measurements reveal that the exchange interactions within the Cu–O planes are very much larger than between the layers, which gives rise to 2-d magnetic behavior, and an overall energy scale which is much larger than the ordering temperatures would suggest. More importantly, these strong spin correlations (and the associated magnetic moments) are also observed in the $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_7$, and $Bi_2Sr_2CaCu_3O_8$ superconducting phases. The correlation range is found to be much shorter in the superconducting state, but the amplitude of the magnetic moment is not diminshed substantially. Recent results on these fluctuations can be found in this conference proceedings [16]. All of these observations of magnetic fluctations in the superconducting state have given credence to models of the superconducting state based on magnetic interactions. It is clear that any comprehensive theory of the oxides must satisfactorily account for both the magnetic as well as the superconducting properties.

## 3. Rare earth magnetism

The majority of the studies of rare earth magnetism have been carried out on the $\mathcal{R}Ba_2Cu_3O_{6+x}$ materials. Some of the very first data showed that substitution of the trivalent rare earths had little effect on the super-

conducting properties, and hence the 4f electrons are effectively isolated from the Cu–O superconducting layers, as well as from each other. Dipolar interactions are then very important in these materials, and the ordering temperatures are tyically a few degrees K or less just like conventional "magnetic-superconductor" systems [3]. The present oxide superconductors should be model systems for studying these interactions in detail.

In the 1-2-3 system there is only one rare earth ion per chemical unit cell, and with $a \approx b$ while $c \approx 3a$, the interactions are expected to be much stronger in the $a$-$b$ plane. The first neutron measurements to be carried out were on $ErBa_2Cu_3O_7$, and the 2-d nature of the scattering which was observed [17, 18] was expected. This anisotropy of the interactions has been recently confirmed on single crystal samples, and in fact this system appears to be an ideal representation of a $S = \frac{1}{2}$, 2-d Ising system. Figure 4 shows a measurement of the magnetic order parameter, where the solid curve is the exact Onsager result [19]. A number of specific heat studies [20] have also indicated 2-d Ising behavior in this system, and 2-d behavior has also been observed in recent neutron scattering measurements [21] on the $\mathcal{R}Ba_2Cu_4O_8$ materials.

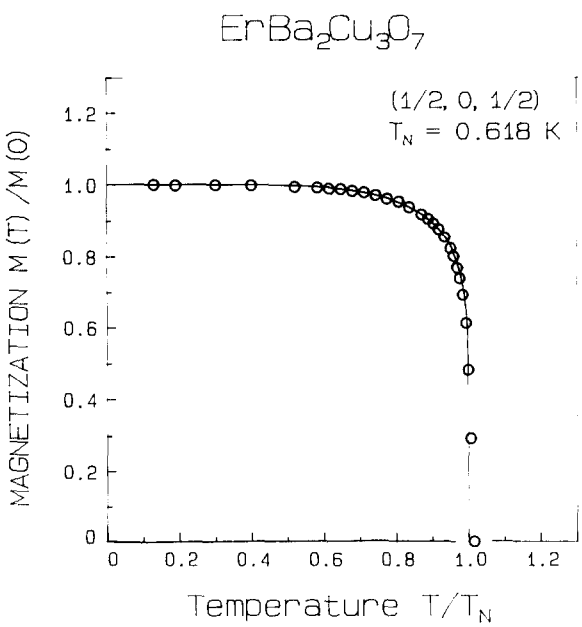


Fig. 4. Sublattice magnetization versus temperature. The solid curve is a fit to Onsager's exact solution for the $S = \frac{1}{2}$, 2-d Ising model.

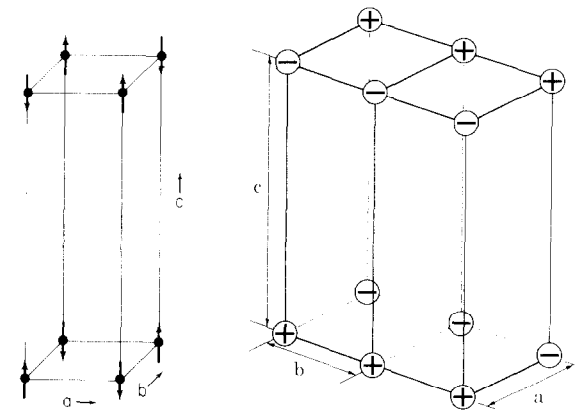


Fig. 5. On the left is the magnetic structure for the Nd, Gd, Dy and Pr rare earth ions in $\mathcal{R}Ba_2Cu_3O_{6+\gamma}$. On the right is the magnetic structure for the Er system.

One of the interesting features of 2-d systems is that they will order three dimensionally even if the interaction in the third direction is very weak [22]. The magnetic structures which have been observed in these materials are shown in fig. 5. The $ErBa_2Cu_3O_7$ structure (right) corresponds to chains of moments which are aligned ferromagnetically along the $b$-axis, while adjacent chains are aligned antiparallel to form an overall antiferromagnetic configuration [18]. In some samples, however, the spins along the $c$-axis are found to be parallel rather than antiparallel, forming ferromagnetic sheets of spins [23]. The dipole energies for these two configurations are very similar, and the specific structure may depend on the metallugical state of the sample. For the Dy [24], Gd [25], Nd [26], and Pr [5] systems, on the other hand, a simple antiferromagnetic structure as shown on the left side has been found. For the Gd system, though, a chain-like structure similar to the Er system has also been observed [27]. Hence the multiplicity of magnetic structures may be a common feature of these systems.

The tetravalent rare earths (Ce, Pr, Tb), on the other hand, are more strongly coupled to the rest of the electronic system, affecting both the superconducting behaviour and the magnetism. The Pr material forms the same orthorhombic structure as $YBa_2Cu_3O_7$, but is thought to be strongly mixed valent, and close to the tetravalent ionic state. The superconductivity is found to be strongly suppressed as a function of Pr concentration [4], and superconductivity is lost for Pr concentrations greater than 60%. The magnetic structure for the Pr is the same as that for Dy, Gd, and Nd, but the ordering temperature of

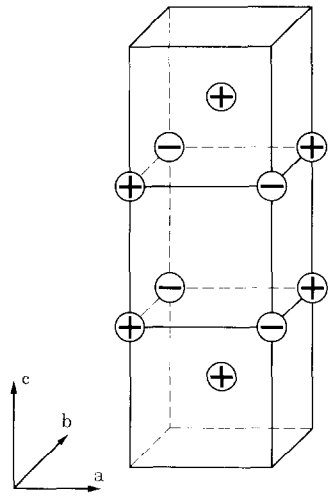


Fig. 6. Magnetic structure for the Nd in $Nd_2CuO_4$.

17 K is much higher than for the trivalent rare earths [5]. The inelastic neutron spectra show [28] a broad distribution of scattering similar to other mixed-valent systems, and the electronic coefficient $\gamma$ obtained from low temperature specific heat measurements is $\sim 200\,mJ/mol\,K^2$ [5], which is comparable to many heavy fermion systems. These observations indicate that the f-electrons in these tetravalent materials are strongly hybridized, and play an essential role in the electronic properties.

Finally we turn to measurements of the magnetic order of Nd in $Nd_2CuO_4$. Again the Nd ions are weakly coupled together, and the ordering temperature is ~1.5 K [29]. The magnetic structure is shown in fig. 6, and is a simple commensurate configuration. However, the data show that the Cu sublattice produces a strong polarization of the Nd ions, and hence it is not a good assumption that the Nd and Cu sublattices are isolated from one another. The Nd polarization is not present when Ce is substituted and the system becomes superconducting, since the Cu sublattice remains magnetically disordered in this case. The Nd sublattice does still order at low temperatures and should polarize the Cu sublattice, and it will be interesting to determine if the superconducting properties are strongly influenced by this ordering.

## Acknowledgements

I would like to thank my many collaborators who have worked on these problems with me. The research at the University of Maryland is supported by the National Science Foundation under grant DMR 86-20269.

## References

[1] See, for example, P.H. Hor, R.L. Meng, Y.Q. Wang, L. Gao. Z.J. Huang, J. Bechtold, K. Forster and C.W. Chu, Phys. Rev. Lett. 58 (1987) 1891.

[2] D.E. Morris, J.H. Nickel, J.Y.T. Wei, N.G. Asmar, J.S. Scott, U.M. Scheven, C.T. Hultgren, A.G. Markelz, J.E. Post, P.J. Heaney, D.R. Veblen and R.M. Hazen, Phys. Rev. B 39 (1989) 7347.

[3] For a review see: Ø. Fischer and M.B. Maple, eds., Topics in Current Physics, Vols. 32 and 34 (Springer, New York, 1983).

[4] L. Soderholm, K. Zhang, D.G. Hinks, M.A. Beno, J.D. Jorgensen, C.U. Segre and I.K. Schuller, Nature 328 (1987) 604.
J.K. Liang, X.T. Xu, S.S. Xie, G.H. Rao, X.Y. Shao and Z.G. Duan, Z. Phys. B 69 (1987) 137.
Y. Dalichaouch, M.S. Torikackvili, E.A. Early, B.W. Lee, C.L. Seaman, K.N. Yang, H. Zhou and M.B. Maple, Solid State Commun. 65 (1988) 1001.

[5] W.-H. Li, J.W. Lynn, S. Skanthakumar, T.W. Clinton, A. Kebede, C.-S. Jee, J.E. Crow and T. Mihalisin, Phys. Rev. B 40 (1989) 5300.

[6] A review of both theory and experiment which pertain to the oxide superconductors is given in: High Temperature Superconductivity, J.W. Lynn, ed. (Springer, New York 1989). The magnetic properties are reviewed in Chap 8.

[7] D.C. Johnston, J.P. Stokes, D.P. Goshorn and J.T. Lewandowshi, Phys. Rev. B 36 (1987) 4007.

[8] See, for example, D. Vaknin, S.K. Sinha, D.E. Moncton, D.C. Johnston, J.M. Newsam, C.R. Safinya and H.E. King, Jr., Phys. Rev. Lett. 58 (1987) 2802.

[9] Y.J. Uemura, C.E. Stronach, D.C. Johnston, M.S. Alvarez and D.P. Goshorn, Phys. Rev. Lett. 59 (1987) 1045.

[10] See, for example, J.M. Tranquada, D.E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S.K. Sinha, M.S. Alverez, A.J. Jacobson and D.C. Johnston, Phys. Rev. Lett. 60 (1988) 156.
W.-H. Li, J.W. Lynn, H.A. Mook, B.C. Sales and Z. Fisk, Phys. Rev. B 37 (1988) 9844.
H. Kadowaki, M. Nishi, Y. Yamada, H. Takeya, H. Takei, S. Shapiro and G. Shirane, Phys. Rev. B 37 (1988) 7932.
J.W. Lynn, W.-H. Li, H.A. Mook, B.C. Sales and Z. Fisk, Phys. Rev. Lett. 60 (1988) 2781.

[11] S. Skanthakumar, H. Zhang, T.W. Clinton, W.-H. Li, J.W. Lynn, Z. Fisk and S.-W. Cheong, Physica C 160 (1989) 124.
Y. Endoh, M. Matsuda, K. Yamada, K. Kakurai, Y.

Hidaka, G. Shirane and R.J. Birgeneau, Phys. Rev. B 40 (1989) 7023.
P. Allenspach, S.-W. Cheong, A. Dommann, P. Fischer, Z. Fisk, A. Furrer, H.R. Ott and B. Rupp, Z. Phys. B, to be published.
D.E. Cox, A.I. Goldman, M.A. Subramanian, J. Gopalakrishnan and A.W. Sleight, Phys. Rev. B 40 (1989) 6998.

[12] G. Shirane, Y. Endoh, R.J. Birgeneau, M.A. Kastner, Y. Hidaka, M. Oda, M. Suzuki and T. Murakami, Phys. Rev. Lett. 59 (1987) 1613.
G. Shirane, R.J. Birgeneau, Y. Endoh, P. Gehring, M.A. Kastner, K. Kitazawa, H. Kojima, I. Tanaka, T.R. Thurston and K. Yamada, Phys. Rev. Lett. 63 (1989) 330.

[13] K.B. Lyons and P.A. Fleury, J. Appl. Phys. 64 (1988) 6075.

[14] Note that for the (nominally) tetragonal $Nd_2CuO_4$ system the $c$-axis is designated as the tetragonal axis. For the $La_2CuO_4$ system, which is orthorhombic at low temperatures, the customary crystallographic notation designates the $b$-axis as the pseudo-tetragonal axis, while $a$ and $c$ are rotated by 45° and multiplied by $\sqrt{2}$.

[15] J.W. Lynn, W.-H. Li, S. Trevino and Z. Fisk, Phys. Rev. B 40 (1989) 5172.

[16] S.M. Hayden, G. Aeppli, H.A. Mook, Z. Fisk, S.-W. Cheong, J.P. Remeika, G.P. Espinosa and A.S. Cooper, Physica B 163 (1990) 1 (these Proceedings).
J. Rossat-Mignod, L.P. Regnault, M.J. Jurgens, C. Vettier, P. Burlet, J.Y. Henry and G. Lapertot, Physica B 163 (1990) 4 (these Proceedings).
T.E. Mason, H. Lin, M.F. Collins, W.J.L. Buyers, A.A. Menovsky and J.A. Mydosh, Physica B 163 (1990) 45 (these Proceedings).

[17] J.W. Lynn, W.-H. Li, Q. Li, H.C. Ku, H.D. Yang and R.N. Shelton, Phys. Rev. B 36 (1987) 2374.

[18] J.W. Lynn, T.W. Clinton, W.-H. Li, R.W. Erwin, J.Z. Liu, R.N. Shelton and P. Klavins, Phys. Rev. Lett. 63 (1989) 2606.

[19] L. Onsager, Phys. Rev. 65 (1944) 117.

[20] See, for example, J. van den Berg, C.J. van der Beek, P.H. Kes, J.A. Mydosh, G.J. Nieuwenhuys and L.J. de Jongh, Solid State Commun. 64 (1987) 699.
S. Simizu, S.A. Friedberg, E.A. Hayri and M. Greenblatt, Phys. Rev. B 36 (1987) 7129.
M.W. Dirken and L.J. de Jongh, Solid State Commun. 64 (1987) 1201.

[21] H. Zhang, J.W. Lynn, W.-H. Li, R.W. Erwin, D.E. Morris and R. Sid, Phys. Rev. B, to be published.

[22] See, for example, R.J. Birgeneau, H.J. Guggenheim and G. Shirane, Phys. Rev. B 1 (1970) 2211.

[23] T. Chattopadhyay, P.J. Brown, B.C. Sales, L.A. Boatner, H.A. Mook and H. Maletta, Phys. Rev. B 40 (1989) 2624.

[24] A.I. Goldman, B.X. Yang, J. Tranquada, J.E. Crow and C.-S. Jee, Phys. Rev. B 36 (1987) 7234.

[25] H.A. Mook, D. McK. Paul, B.C. Sales, L.A. Boatner and L. Cussen, Phys. Rev. B 38 (1988) 12008.

[26] K.N. Yang, J.M. Ferreira, B.W. Lee, M.B. Maple, W.-H. Li, J.W. Lynn and R.W. Erwin, Phys. Rev. B 40 (1989) 10963.
P. Fischer, B. Schmid, P. Bruesch, F. Stucki and P. Unternahrer, Z. Phys. B 74 (1989) 183.

[27] T. Chattopadhyay, H. Maletta, W. Wirgen, K. Fischer and P.J. Brown, Phys. Rev. B 38 (1988) 838.

[28] S. Skanthakumar, W.-H. Li, J.W. Lynn, A. Kebede, J.E. Crow and T. Mihalisin, Physica B 163 (1990) 239 (these Proceedings).

[29] J.W. Lynn, I.W. Sumarlin, S. Skanthakumar, W.-H. Li, Z. Fisk, S.-W. Cheong, R.N. Shelton and J.L. Peng, Phys. Rev. B 41 (1990), to be published.